Structure of Polymer Solutions in Poor Solvents

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It is generally believed that deterioration of the solvent quality (e.g. decreasing the temperature) must lead to a substantial reduction in the dimensions of polymer coils. For dilute solutions, this effect is well documented both theoretically and experimentally for the crossover from a good solvent to a theta (Q) solvent and also from the Q condition to a poor solvent regime. Much less is known about the conformation of chains in semidilute domain at temperatures T < Q down to the critical temperature of phase demixing, T^c. We present and discuss results of the first measurements of the radius of gyration (R_p) for semiflexible polymers in the poor solvent region over a temperature range Q ³ T ³ T^c using small-angle neutron scattering. To extract the single-chain and the total structure factor we also make use of high-concentration (isotopic) labeling which allows us to substantially increase the signal-to-noise ratio. We have studied mixtures of normal (H-labeled) and deuterated (D-labeled) polystyrene with virtually identical molecular weight in deuterocyclohexane at the critical polymer concentration. We find that reduction of temperature leads to divergence of the correlation length x in the vicinity of the critical point of phase demixing. By contrast, the radius of gyration of polymer chains remains unperturbed below the Q temperature down to T^c, and the abrupt decrease of $R_{\mathfrak{g}}$ is revealed only at $T < T^{\mathfrak{c}}$ along the dilute branch of the spinodal. We thus conclude that, contrary to some theoretical predictions, the critical polymer solution does not behave as an assembly of partially collapsed noninterpenetrating coils, but rather as an ensemble of microdomains of the size x representing unperturbed, strongly interpenetrating polymers.